

# On highly accurate calculations of the excited $n^1S(L = 0)$ -states in helium atoms

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## Abstract

The total energies and various bound state properties of the excited  $2^1S(L = 0)$ -states in two-electron helium atoms, including the  ${}^\infty\text{He}$ ,  ${}^4\text{He}$  and  ${}^3\text{He}$  atoms, are determined to very high numerical accuracy. The convergence of the results obtained for some electron-nuclear and electron-electron expectation values and, in particular, for the electron-nuclear and electron-electron cusp values, is discussed. The field component of the isotope shift and lowest order QED correction are estimated for the  $2^1S(L = 0)$ -states in the  ${}^4\text{He}$  and  ${}^3\text{He}$  atoms. We also apply our highly accurate methods to numerical computations of the excited  $n^1S$ -states (for  $n = 3$  and 4) in two-electron atomic systems.

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## I. INTRODUCTION

In this communication we consider the bound state properties of the excited  $2^1S(L = 0)$ -states in two-electron helium atoms:  ${}^\infty\text{He}$ ,  ${}^4\text{He}$  and  ${}^3\text{He}$ . In our previous work [1] we have performed highly accurate computations for the ground  $1^1S(L = 0)$ -state and for the triplet  $2^3S(L = 0)$ -states in a number of helium-like ions. Another work [2] contains highly accurate results for the singlet  $2^1P(L = 1)$ - and triplet  $2^3P(L = 1)$ -states in helium atom(s). In this study we want to consider the excited  $2^1S(L = 0)$ -states in two-electron helium atoms. Our current interest to the excited  $2^1S(L = 0)$ -states in the He atoms stems from the following. First, many bound state properties of the excited  $2^1S(L = 0)$ -states in helium atoms have not been computed in earlier studies (see, e.g., [3], [4] and references therein).

Second, there is a common believe that construction of highly accurate wave functions for the excited states in two-electron atoms and ions is a significantly more complicated process than in the case of the lowest states with the same  $L$  and  $S$  quantum numbers. Here and below the notations  $L$  and  $S$  designate the quantum numbers of total angular momentum and electron spin, respectively (see, e.g., [5] and [6]). Most of the expected complications most likely arise from various numerical instabilities which become crucial during optimization of the non-linear parameters in the wave functions. Indeed, the repeated optimization and re-optimization of the non-linear parameters in the wave function is a potentially unstable process for the excited states. Formally, by optimizing these parameters we are trying to decrease the second, third, ...,  $n - th$  eigenvalue, i.e. the second, third, etc, root of the eigenvalue equation. The orthogonality of the wave functions of the excited states to the wave function of the ground state is not checked during such an optimization. This means that after a few steps of the optimization of non-linear parameters the process of construction of a highly accurate wave function for an excited state may begin to converge to the ground state wave function. This ‘instability’ problem explains a relatively modest progress achieved in highly accurate calculations of the excited states in comparison to the ground state.

Third, it is commonly assumed that, for some unexplained reasons, the overall convergence rate for bound state properties of the excited atomic states will be substantially lower than analogous convergence rate for the same properties determined for the lowest energy state with the same  $L$  and  $S$  numbers. This problem has not been studied carefully in earlier

works. It can be answered by computing a large number of bound state properties for the excited  $2^1S$ -state in the He atom(s) with the use of different number of basis functions.

## II. METHOD

Our computational goal in this study is to determine the highly accurate solutions, i.e. the eigenstates and corresponding wave functions, of the non-relativistic Schrödinger equation  $H\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ , where  $E < 0$  [7], for  $2^1S(L = 0)$ -state(s) in the neutral helium atom. For an arbitrary two-electron atomic system with the nuclear charge  $Qe$  the non-relativistic Hamiltonian is written in the following form

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\left(\frac{m_e}{M}\right)\nabla_3^2 - \frac{Qe^2}{r_{32}} - \frac{Qe^2}{r_{31}} + \frac{e^2}{r_{21}} , \quad (1)$$

where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = r_{ji}$  ( $i \neq j = (1, 2, 3)$ ) and  $\mathbf{r}_i$  is the radius-vector of the  $i$ -th particle written in Cartesian coordinates. Also, in this equation  $\nabla_i = \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i}\right)$  is the gradient operator for the particle with index  $i$  ( $i = 1, 2, 3$ ). Here and everywhere below in this study the subscripts 1 and 2 designate the two electrons, while the subscript 3 stands for the nucleus. In the Hamiltonian, Eq.(1),  $Q = q_3$  is the nuclear charge, while  $M = m_3 \gg 1$  is the nuclear mass. In atomic units where  $\hbar = 1, e = 1, m_e = 1$  the Hamiltonian  $H$ , Eq.(1), takes the form

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M}\nabla_3^2 - \frac{Q}{r_{32}} - \frac{Q}{r_{31}} + \frac{1}{r_{21}} , \quad (2)$$

In this study the unknown wave functions are approximated with the use of exponential variational expansion in relative coordinates  $r_{32}, r_{31}$  and  $r_{21}$ . For the excited  $2^1S(L = 0)$ -states, the exponential variational expansion for the spatial part of an arbitrary two-electron wave function takes the form [8]

$$\begin{aligned} \Psi_{LM} &= \frac{1}{\sqrt{2}}(1 + \hat{P}_{21}) \sum_{i=1}^N C_i \exp(-\tilde{\alpha}_i u_1 - \tilde{\beta}_i u_2 - \tilde{\gamma}_i u_3) \\ &= \frac{1}{\sqrt{2}}(1 + \hat{P}_{21}) \sum_{i=1}^N C_i \exp(-\alpha_i r_{32} - \beta_i r_{31} - \gamma_i r_{21}) \end{aligned} \quad (3)$$

where  $C_i$  are the linear (or variational) parameters,  $\alpha_i, \beta_i$  and  $\gamma_i$  are the non-linear parameters ( $i = 1, 2, \dots, N$ ) of variational expansion, Eq.(3). The operator  $\hat{P}_{21}$  is the permutation of the two identical (1 and 2) particles (electrons) in the symmetric two-electron ions. In

this equation  $u_1, u_2, u_3$  are the three perimetric coordinates which are truly independent and simply related to the three relative coordinates:  $u_i = \frac{1}{2}(r_{ik} + r_{ij} - r_{jk})$ . The inverse relation takes the form  $r_{ij} = u_i + u_j$ , where  $(i, j, k) = (1, 2, 3)$ . Note that each of the perimetric coordinates varies between 0 and  $+\infty$ .

In general, by using the variational expansion, Eq.(3), it is possible to construct extremely accurate wave functions for the  $S(L = 0)$ -states in arbitrary three-body systems, if (and only if) the non-linear parameters  $\alpha_i, \beta_i$  and  $\gamma_i$  in Eq.(3) are varied. In this study we shall use the numerical methods and optimization strategy developed in our earlier work [8]. The procedure developed in [8] allows one to produce extremely accurate (or essentially exact) variational results for arbitrary three-body systems, including the  $\text{Ps}^-$  and  $\text{H}^-$  ions [9]. Many of these systems, however, have either one ground bound  $1^1S$ -state, or a few bound states with different  $L$  and  $S$  quantum numbers. For two-electron atoms and ions which have infinite numbers of excited states we modified our strategy developed in [8] to provide a better numerical stability during each step of optimization.

### III. PROPERTIES

The results of our variational calculations for the excited  $2^1S(L = 0)$ -state in the helium atom with infinitely heavy nucleus, i.e. in the  ${}^\infty\text{He}$  atom, can be found in Table I which contains the total energies  $E$  and  $\langle r_{21} \rangle, \langle \delta_{31} \rangle$  and  $\nu_{31}$  expectation values expressed in atomic units. The notations  $\langle r_{21} \rangle, \langle \delta_{31} \rangle$  and  $\nu_{31}$  are explained below. These expectation values have been determined with the use of trial wave functions with the different number of basis functions  $N$ . In this study to approximate the highly accurate wave functions we have used the exponential variational expansion in relative coordinates  $r_{32}, r_{31}$  and  $r_{21}$ , Eq.(3).

Table II contains the expectation values of many atomic properties of the  $2^1S$ -state (expressed in atomic units or *a.u.*) determined using the most accurate wave functions obtained in this study. The physical meaning of almost all of the expectation values presented in Tables I and II is clear, and we make here only a few following remarks. The expectation values of interparticle distances and their powers are designated as  $\langle r_{ij}^k \rangle$  for  $k = 1, 2, 3, 4; -1, -2$  and  $(ij) = (31), (21)$  for the two-electron He atom. The expectation values of the electron-nuclear, electron-electron and triple delta-functions are designated as  $\langle \delta(\mathbf{r}_{31}) \rangle = \langle \delta_{31} \rangle, \langle \delta(\mathbf{r}_{21}) \rangle = \langle \delta_{21} \rangle, \langle \delta(\mathbf{r}_{321}) \rangle = \langle \delta(\mathbf{r}_{32})\delta(\mathbf{r}_{31}) \rangle = \langle \delta_{321} \rangle$ . Also, Tables I and II

include the electron-nuclear ( $\nu_{31}$ ) and electron-electron ( $\nu_{21}$ ) cusp values [10], [11]:

$$\nu_{ij} = \frac{\langle \delta(\mathbf{r}_{ij}) \frac{\partial}{\partial r_{ij}} \rangle}{\langle \delta(\mathbf{r}_{ij}) \rangle} \quad (4)$$

where  $\delta(\mathbf{r}_{ij}) = \delta_{ij}$  is the appropriate delta-function and  $(ij) = (31), (21)$ . In this study we shall assume that all point particles interact with each other by the Coulomb potentials. Therefore, the expected (exact) two-particle cusp equals  $\nu_{ij} = q_i q_j \frac{m_i m_j}{m_i + m_j}$  [10], [11], where  $q_i, q_j$  are the particle's charges and  $m_i, m_j$  are their masses. For the considered singlet  $2^1S(L=0)$ -states in the two-electron helium atom with the infinitely heavy nucleus  ${}^\infty\text{He}$ , the expected electron-nuclear cusp equals  $-Q = -2$ , while the electron-electron cusp equals 0.5. For the  ${}^3\text{He}$  and  ${}^4\text{He}$  helium atoms the electron-electron cusps also equal 0.5 (exactly), while electron-nuclear cusps include some small correction for the  $\frac{m_e}{M} = \frac{1}{M}$  ratio. For the  ${}^3\text{He}$  and  ${}^4\text{He}$  helium atoms one finds for the electron-nuclear cusp (in atomic units)

$$\nu_{31} = -Q \frac{M}{M+1} = -Q \left(1 - \frac{1}{M+1}\right) \quad (5)$$

where  $M \gg 1$  and  $Q$  is the nuclear electric charge. In our calculations of the  $2^1S$ -states in the  ${}^3\text{He}$  and  ${}^4\text{He}$  helium atoms the following values of nuclear mass were used:  $M({}^3\text{He}) = 5495.8852 m_e$  and  $M({}^4\text{He}) = 7294.2996 m_e$  [12], [13].

The coincidence between the expected and computed cusp values provides a very convenient, accurate and universal criterion to control the overall quality of the wave function constructed in our computations. In general, the electron-electron cusp is a better criterion of the overall quality of the variational wave function than the electron-nuclear cusp. This means that in actual calculations it is much harder to obtain a good/excellent agreement for the electron-electron cusp, than a similar agreement for the electron-nuclear cusp.

Table II also contains the expectation values of the two interparticle *cosine*-functions which are determined as follows

$$\tau_{ij} = \langle \cos(\mathbf{r}_{ik} \wedge \mathbf{r}_{jk}) \rangle = \left\langle \frac{\mathbf{r}_{ik} \cdot \mathbf{r}_{jk}}{r_{ik} r_{jk}} \right\rangle , \quad (6)$$

where  $(i, j, k) = (1, 2, 3)$ . The  $\tau_{ij}$  expectation values are always  $\leq 1$ . The absolute value of  $\tau_{21} (\equiv \tau_{12})$  can be considered as an ‘ideal’ measure of the static electron-electron correlations in the two-electron atomic systems. Let us define the quantity  $\langle f \rangle$  which is expressed in terms of the relative coordinates  $(r_{31}, r_{32}, r_{21})$  or perimetric coordinates  $(u_1, u_2, u_3)$  as follows:

$$\langle f \rangle = \frac{1}{2} \langle \psi | \frac{u_1}{r_{32}} \frac{u_2}{r_{31}} \frac{u_3}{r_{21}} | \psi \rangle = \iiint |\psi(u_1, u_2, u_3)|^2 u_1 u_2 u_3 du_1 du_2 du_3 . \quad (7)$$

It can be shown that the equality

$$\tau_{21} + \tau_{32} + \tau_{31} = 1 + 4\langle f \rangle \quad (8)$$

holds for arbitrary three-body system. For the two-electron (i.e. symmetric) ions/atoms we always have  $\tau_{32} = \tau_{31}$ , and therefore,  $\tau_{21} + 2\tau_{31} = 1 + 4\langle f \rangle$ . It can be also shown that in an arbitrary Coulomb three-body system  $0 \leq \langle f \rangle < 0.085$ . The  $\langle f \rangle$  value can be calculated either directly from Eq.(7), or by applying the expectation values of the *cosine* functions  $\tau_{ij}$  computed earlier. The coincidence of these two values of  $\langle f \rangle$  indicates that the  $\tau_{32}, \tau_{31}, \tau_{21}$  and  $\langle f \rangle$  expectation values have been computed correctly.

The virial factor  $\eta$  in Table II is determined as follows:

$$\eta = |1 + \frac{\langle V \rangle}{2\langle T \rangle}| \quad (9)$$

where  $\langle T \rangle$  and  $\langle V \rangle$  are the expectation values of the kinetic and potential energy, respectively. The deviation of the factor  $\eta$  from zero indicates, in principle, the overall quality of the variational wave function used [14]. In particular, for the wave functions used in our present calculations, the virial parameters  $\eta$  is in the range  $1 \cdot 10^{-18} - 5 \cdot 10^{-19}$ , showing that our wave functions are highly accurate.

Note that some of the bound state properties from Table II can be expressed as the linear combinations of other properties. For instance, by using the identity

$$\mathbf{r}_{31} = \mathbf{r}_{32} - \mathbf{r}_{21} \quad (10)$$

one finds for the  $\langle \mathbf{r}_{31} \cdot \mathbf{r}_{32} \rangle$  and  $\langle \mathbf{r}_{31} \cdot \mathbf{r}_{32} \rangle$  expectation values

$$\langle \mathbf{r}_{31} \cdot \mathbf{r}_{32} \rangle = \frac{1}{2}(\langle r_{32}^2 \rangle + \langle r_{31}^2 \rangle - \langle r_{21}^2 \rangle) \quad (11)$$

and

$$\langle \mathbf{r}_{21} \cdot \mathbf{r}_{32} \rangle = \frac{1}{2}(\langle r_{32}^2 \rangle + \langle r_{21}^2 \rangle - \langle r_{31}^2 \rangle) \quad (12)$$

here and everywhere below the notation  $\mathbf{a} \cdot \mathbf{b}$  stands for the scalar product of the  $\mathbf{a}$  and  $\mathbf{b}$  vectors, i.e.  $\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z$ , where  $\mathbf{a} = (a_x, a_y, a_z)$  and  $\mathbf{b} = (b_x, b_y, b_z)$ . Analogously, since  $(\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3) |\Psi\rangle = 0$ , we have

$$\langle \mathbf{p}_i \cdot \mathbf{p}_j \rangle = \frac{1}{2}(\langle p_i^2 \rangle + \langle p_j^2 \rangle - \langle p_k^2 \rangle) \quad (13)$$

where  $(i, j, k) = (1, 2, 3)$ . In the gradient form this equality takes the form

$$\langle \nabla_i \cdot \nabla_j \rangle = \frac{1}{2}(\langle \nabla_i^2 \rangle + \langle \nabla_j^2 \rangle - \langle \nabla_k^2 \rangle) = -\langle -\frac{1}{2}\nabla_i^2 \rangle - \langle -\frac{1}{2}\nabla_j^2 \rangle + \langle -\frac{1}{2}\nabla_k^2 \rangle \quad (14)$$

where  $\langle -\frac{1}{2}\nabla_i^2 \rangle$  ( $i = 1, 2, 3$ ) are the single-particle kinetic energies. In the general case, the both sides of the equalities Eqs.(13) - (14) can be computed separately, i.e. such relations can be also used to control the overall quality of the variational wave function. The  $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$  expectation value can also be used as a measure of the dynamical electron-electron correlation in the two-electron ions. It should be noticed that there is an obvious difference between the  $\langle \mathbf{p}_1 \Psi | \mathbf{p}_2 \Psi \rangle$  and  $\langle \Psi | \mathbf{p}_1 \cdot \mathbf{p}_2 | \Psi \rangle$  expectation values. In fact, these two expectation values differ from each other by sign, i.e.  $\langle \mathbf{p}_1 \Psi | \mathbf{p}_2 \Psi \rangle = -\langle \Psi | \mathbf{p}_1 \cdot \mathbf{p}_2 | \Psi \rangle$ .

### A. Singular expectation values

All expectation values mentioned above are regular, i.e. their analytical and/or numerical computation is relatively simple. A few expectation values from Table II, however, contain some singular parts. In such cases some additional explanations are needed. For instance, consider the expectation value  $\langle \frac{1}{r_{32}} \rangle = \langle \frac{1}{r_{31}} \rangle$ . In relative coordinates  $r_{32}, r_{31}, r_{21}$  the computation of this expectation value is reduced to the calculation of the following Hylleraas-type integrals

$$\Gamma_{-2,1,1}(a, b, c) = \int_0^\infty \int_0^\infty \int_{|r_{32}-r_{31}|}^{r_{32}+r_{31}} \exp(-ar_{32} - br_{31} - cr_{21}) r_{32}^{-2} r_{31} r_{21} dr_{32} dr_{31} dr_{21} \quad (15)$$

for many different sets of  $(a, b, c)$ -values. Formally, each of these integrals diverges, i.e. it does not exist as a finite expression. To make this integral finite one needs to introduce a small (and positive) cutoff parameter  $\epsilon$

$$\Gamma_{-2,1,1}(a, b, c; \epsilon) = \int_\epsilon^\infty \int_0^\infty \int_{|r_{32}-r_{31}|}^{r_{32}+r_{31}} \exp(-ar_{32} - br_{31} - cr_{21}) r_{32}^{-2} r_{31} r_{21} dr_{32} dr_{31} dr_{21} \quad (16)$$

Now, this integral is finite for  $\epsilon > 0$ , but diverges when  $\epsilon \rightarrow 0$ . For the finite integral  $\Gamma_{-2,1,1}(a, b, c; \epsilon)$  defined by Eq.(16) for  $\epsilon > 0$  we can write

$$\Gamma_{-2,1,1}(a, b, c; \epsilon) = \frac{\partial^2 \Gamma_{-2,0,0}(a, b, c; \epsilon)}{\partial b \partial c} \quad (17)$$

where

$$\Gamma_{-2,0,0}(a, b, c; \epsilon) = \int_\epsilon^\infty \int_0^\infty \int_{|r_{32}-r_{31}|}^{r_{32}+r_{31}} \exp(-ar_{32} - br_{31} - cr_{21}) r_{32}^{-2} dr_{32} dr_{31} dr_{21} \quad (18)$$

The  $\Gamma_{-2,0,0}(a, b, c; \epsilon)$  integral is represented as the sum of its regular ( $R$ ) and singular ( $S$ ) parts, i.e.  $\Gamma_{-2,0,0}(a, b, c; \epsilon) = R_{-2,0,0}(a, b, c) + S_{-2,0,0}(a, b, c; \epsilon)$ , where

$$S_{-2,0,0}(a, b, c; \epsilon) = \frac{2}{b+c} (\psi(1) - \ln\epsilon) = -\frac{2}{b+c} (\gamma_E + \ln\epsilon) \quad (19)$$

$$\begin{aligned} R_{-2,0,0}(a, b, c) &= 2 \frac{(a+c)\ln(a+c) - (a+b)\ln(a+b)}{(b^2 - c^2)} + \frac{2}{b+c} \\ &= R_{-2,0,0}^{(\ln)}(a, b, c) + F_{-2,0,0}(a, b, c) \end{aligned} \quad (20)$$

where  $\psi(n)$  is the digamma function [15] (or *psi*-function defined in Eq.(8.360) from [16]). Note that  $\psi(1) = -\gamma_E$ , where  $\gamma_E \approx 0.577215\dots$  is the Euler's constant. The  $R_{-2,0,0}^{(\ln)}(a, b, c)$  term is the 'logarithmic' term which contains the  $\ln(a+c)$  and  $\ln(a+b)$  expressions, i.e.

$$R_{-2,0,0}^{(\ln)}(a, b, c) = \frac{2}{(b^2 - c^2)} [(a+c)\ln(a+c) - (a+b)\ln(a+b)] ,$$

while

$$F_{-2,0,0}(a, b, c) = \frac{2}{b+c}$$

The second order derivative of the regular part is

$$R_{-2,1,1}(a, b, c) = \frac{\partial^2 R_{-2,0,0}^{(\ln)}(a, b, c)}{\partial b \partial c} + \frac{4}{(b+c)^3} \quad (21)$$

The expectation values of both sides of this equation are

$$\langle \Psi | R_{-2,1,1}(a, b, c) | \Psi \rangle = \langle \Psi | \frac{\partial^2 R_{-2,0,0}^{(\ln)}(a, b, c)}{\partial b \partial c} | \Psi \rangle + \langle \Psi | \frac{4}{(b+c)^3} | \Psi \rangle \quad (22)$$

In the exponential basis the  $\frac{4}{(b+c)^3}$  matrix elements correspond to the  $\delta(\mathbf{r}_{32})$  delta-function multiplied by a factor of  $4\pi$ . The corresponding expectation value is

$$\langle \Psi | R_{-2,1,1}(a, b, c) | \Psi \rangle = \langle \Psi | \frac{\partial^2 R_{-2,0,0}^{(\ln)}(a, b, c)}{\partial b \partial c} | \Psi \rangle + 4\pi \langle \delta(\mathbf{r}_{32}) \rangle \quad (23)$$

Analogously, the expectation value of the singular part is

$$\langle \Psi | S_{-2,1,1}(a, b, c; \epsilon) | \Psi \rangle = -4\pi \langle \delta(\mathbf{r}_{32}) \rangle (\gamma_E + \ln\epsilon) \quad (24)$$

where  $\langle \delta(\mathbf{r}_{32}) \rangle$  is the expectation value of the  $\delta(\mathbf{r}_{32})$  delta-function.

As follows from the definition  $\Gamma_{-2,1,1}(a, b, c; \epsilon) = R_{-2,1,1}(a, b, c) + S_{-2,1,1}(a, b, c; \epsilon)$  the sum

$$\Gamma_{-2,1,1}(a, b, c; \epsilon) + S_{-2,1,1}(a, b, c; \epsilon) = R_{-2,1,1}(a, b, c) \quad (25)$$

is the regular expression and it has the finite limit when  $\epsilon \rightarrow 0$ . The limits of both sides of Eq.(25) are

$$\langle \frac{1}{r_{32}^3} \rangle = \lim_{\epsilon \rightarrow 0} \left[ \langle \Psi | \frac{1}{r_{32}^3} | \Psi \rangle_\epsilon + 4\pi \langle \delta(\mathbf{r}_{32}) \rangle (\gamma_E + \ln \epsilon) \right] = 4\pi \langle \delta(\mathbf{r}_{32}) \rangle + \langle \Psi | \frac{1}{r_{32}^3} | \Psi \rangle_R \quad (26)$$

This expression is considered as the expectation value of the  $\frac{1}{r_{32}^3}$  operator, i.e. we have

$$\langle \frac{1}{r_{32}^3} \rangle = 4\pi \langle \delta(\mathbf{r}_{32}) \rangle + \langle \Psi | \frac{1}{r_{32}^3} | \Psi \rangle_R \quad (27)$$

Note that in contrast with the expectation values of regular operators the  $\langle \frac{1}{r_{32}^3} \rangle$  does not coincide with the  $\langle \Psi | \frac{1}{r_{32}^3} | \Psi \rangle_R$  expectation value. The presence of the finite difference  $4\pi \langle \delta(\mathbf{r}_{32}) \rangle$  is typical for the expectation values of singular operators. For the  $\langle \frac{1}{r_{21}^3} \rangle$  expectation value the analogous formula takes the form [17]

$$\langle \frac{1}{r_{21}^3} \rangle = \lim_{\epsilon \rightarrow 0} \left[ \langle \Psi | \frac{1}{r_{21}^3} | \Psi \rangle_\epsilon + 4\pi \langle \delta(\mathbf{r}_{21}) \rangle (\gamma_E + \ln \epsilon) \right] = 4\pi \langle \delta(\mathbf{r}_{21}) \rangle + \langle \Psi | \frac{1}{r_{21}^3} | \Psi \rangle_R \quad (28)$$

Note also that in Eq.(23) the second order derivative is

$$\begin{aligned} \frac{\partial^2 R_{-2,0,0}^{(ln)}(a, b, c)}{\partial b \partial c} &= 16 \frac{[(a+c)\ln(a+c) - (a+b)\ln(a+b)]bc}{(c^2 - b^2)^3} \\ &\quad - 4 \frac{[\ln(a+b) + 1]c}{(b^2 - c^2)^2} - 4 \frac{[\ln(a+c) + 1]b}{(b^2 - c^2)^2} \end{aligned} \quad (29)$$

It is easy to understand that this formula is computationally unstable, when  $c \rightarrow b$ . Indeed, both the numerator and denominator in this formula  $\rightarrow 0$  when  $c \rightarrow b$ . This produces some troubles in actual calculations. The transformation of this formula to the computationally stable form when  $c \rightarrow b$  can be found in [17]. The most detailed analysis of various singular integrals arising in two-electron atomic problems can be found in [18].

#### IV. CORRECTIONS TO THE TOTAL ENERGY

The expectation values from Table II can be used to determine some actual properties of the helium atoms in the  $2^1S$ -state. Here by the ‘actual properties’ we mean some linear combinations of our expectation values which can be measured in modern experiments. The most important of such properties are various lowest order corrections to the total non-relativistic energies. Formally, by computing all possible lowest order corrections, e.g., relativistic and quantum electrodynamics corrections, mass corrections, etc, we must obtain

the exact agreement with the energies measured in high precision experiments. In this Section we consider a few such corrections to the non-relativistic atomic energies of the  $2^1S$ -state in the two-electron helium atom(s).

First, let us evaluate the field component of the total isotope shift for the  $2^1S$ -state in helium atoms. The field shift is related to the extended nuclear charge distribution which produces the non-Coulomb field at distances close to the nucleus. It is clear that the largest deviations between the Coulomb and actual potentials can be found close to the atomic nucleus, i.e. for distances  $r \approx r_e \ll \Lambda \ll a_0$ , where  $r_e = \alpha^2 a_0$  is the classical electron radius and  $\Lambda = \alpha a_0$  is the Compton wave length. Here and below,  $\alpha = 7.297352568 \cdot 10^{-3}$  is the fine structure constant and  $a_0 \approx 5.29177249 \cdot 10^{-11} \text{ m}$  is the Bohr radius. Note that all numerical values for the physical constants used in this study were chosen from [12], [13]. The general theory of the field shift has been discussed extensively in a number of works (see, e.g., [19], [20], [21] and references therein).

In our earlier work [22] we obtained the following expression for the field shift (in atomic units) of the bound  $S(L=0)$ -states in light atoms and ions (with  $Q \leq 6$ )

$$E_M^{fs} = \frac{8\pi}{3} Q \rho_e(0) R^2 \left( \frac{3+\lambda}{5-\lambda} \right) = \frac{8\pi}{5} Q \rho_e(0) R^2 \left( \frac{1+\frac{1}{3}\lambda}{1-\frac{1}{5}\lambda} \right) = \frac{8\pi}{5} Q \alpha^4 \cdot \langle \delta(\mathbf{r}_{eN}) \rangle \left( \frac{R}{r_e} \right)^2 \xi \quad (30)$$

where  $Q$  is the nuclear charge and  $R$  is the nuclear radius. Our formula for the field shift  $E_M^{fs}$  follows from the well known expression obtained by Racah, Rosenthal and Breit (see, e.g., [19]). Its explicit derivation can be found in the Appendix. The parameter  $\lambda$  and related factor  $\xi = \frac{1+\frac{1}{3}\lambda}{1-\frac{1}{5}\lambda}$  in Eq.(30) describe the actual charge/proton distribution in the nucleus. Also, in this expression  $r_e = \frac{e^2}{m_e c^2} = \alpha^2 a_0 \approx 2.81794093 \text{ fm}$  ( $1 \text{ fm}$  (fermi) =  $1 \cdot 10^{-13} \text{ cm}$ ) is the classical electron radius. In general, the nuclear radius  $R \approx r_e$  and its actual value depends upon the total number of nucleons  $A$  in the nucleus ( $R \sim A^{\frac{1}{3}}$ ). In other words, the field shift formally corresponds to the  $\alpha^4$ -correction to the energy levels, i.e. to the second order relativistic correction. Let us evaluate the  $E_M^{fs}$  shifts for the  $2^1S$ -state in the  ${}^3\text{He}$  and  ${}^4\text{He}$  atoms. The nuclear sizes used in our computations were  $R({}^3\text{He}) = 1.880 \text{ fm}$  [23] and  $R({}^4\text{He}) = 1.6773 \text{ fm}$  [24] (see also [25] and [26]). We have also selected zero value for the parameter  $\lambda$ , i.e.  $\xi = 1$  in Eq.(30). This means that the uniform (or  $r$ -independent) proton density distribution over the volume of the nucleus is assumed for each of the  ${}^3\text{He}$  and  ${}^4\text{He}$  nuclei. This assumption produces the following values for the field shifts  $E_M^{fs}({}^3\text{He}) = 1.66061 \cdot 10^{-8} \text{ a.u.}$  and  $E_M^{fs}({}^4\text{He}) = 1.32120 \cdot 10^{-8} \text{ a.u.}$  Numerical recalculation of these values

to  $cm^{-1}$ ,  $MHz$ ,  $eV$  and other units is straightforward.

Another example is the lowest order ( $\sim \alpha^3$ ) QED correction to the non-relativistic energies of the  $2^1S$ -state of the helium atoms. For an arbitrary bound  $S(L = 0)$ -state in the  ${}^\infty\text{He}$  atom the closed analytical formula for the lowest order QED correction is written in the form (in atomic units)

$$\Delta E^{(3)} = \frac{8}{3}Q\alpha^3 \left[ \frac{19}{30} - 2\ln\alpha - \ln K_0 \right] \langle \delta(\mathbf{r}_{31}) \rangle + \alpha^3 \left[ \frac{164}{15} + \frac{14}{3}\ln\alpha - \frac{10}{3}S(S+1) \right] \langle \delta(\mathbf{r}_{21}) \rangle - \frac{14}{3}\alpha^3 \left( \frac{1}{4\pi} \langle \frac{1}{r_{21}^3} \rangle \right) \quad (31)$$

where  $\alpha$  is the fine structure constant,  $Q$  ( $= 2$ ) is the nuclear charge and  $S$  is the total spin of two electrons. For the singlet states we always have  $S = 0$ . Also, in this formula  $\ln K_0$  is the Bethe logarithm [5], which is represented in the form  $\ln K_0 = \ln k_0 + 2\ln Q$ , where  $\ln k_0$  is the charge-reduced Bethe logarithm. Our current numerical evaluation of the charge-reduced Bethe logarithm for the  $2^1S$ -state of the  ${}^\infty\text{He}$  atom is  $\ln k_0 \approx 2.98011831$ . This value is not very accurate and must be improved in future calculations. Therefore, the value of Bethe logarithm for this state is  $\ln K_0 \approx 4.36641267$ . By using this value of  $\ln K_0$  and expectation values from Table II for the one finds that for the  ${}^\infty\text{He}$  atom  $\Delta E^{(3)} \approx 1.1890905 \cdot 10^{-5}$  a.u. This is the lowest order ( $\sim \alpha^3$ ) QED correction determined for the  $2^1S$ -state in the  ${}^\infty\text{He}$  atom.

For the two-electron helium atoms with the finite nuclear masses we need to determine the corresponding finite mass correction (or recoil correction, for short). The recoil correction to the lowest order QED correction in the case of  $S(L = 0)$ -states in two-electron atoms/ions is represented in the form [27] (in atomic units):

$$\Delta E_M^{(3)} = \left( \frac{M}{M+1} - \frac{2}{M} \right) \Delta E^{(3)} + \frac{4\alpha^3}{3M} \left[ \frac{31}{3} + 2 - \ln\alpha - 4\ln K_0 \right] \langle \delta(\mathbf{r}_{31}) \rangle - \frac{2}{M} \cdot \frac{14}{3}\alpha^3 \left( \frac{1}{4\pi} \langle \frac{1}{r_{31}^3} \rangle \right) \quad (32)$$

where  $\Delta E^{(3)}$  is the expression from Eq.(31), while  $M$  ( $M \gg 1$ ) is the nuclear mass (expressed in the electron mass  $m_e$ ). By using our expectation values from Table II and charge-reduced Bethe logarithm determined for the  $2^1S$ -state in the  ${}^\infty\text{He}$  atom one finds from Eq.(32) that  $\Delta E_M^{(3)}({}^4\text{He}) \approx 1.1891233 \cdot 10^{-5}$  a.u. and  $\Delta E_M^{(3)}({}^3\text{He}) \approx 1.1891340 \cdot 10^{-5}$  a.u. To obtain a slightly better accuracy in the last equation we can use the expectation values from Table II determined for the two-electron He atoms with the finite nuclear masses. In these cases one

finds from Eq.(32)  $\Delta E_M^{(3)}(^4\text{He}) \approx 1.1891230 \cdot 10^{-5}$  a.u. and  $\Delta E_M^{(3)}(^3\text{He}) \approx 1.1891319 \cdot 10^{-5}$  a.u.

The last example which we want to consider here is related to the Vinti identity [28]. For two-electron atoms/ions this identity takes the form

$$\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle = \frac{Q}{2} \langle \mathbf{r}_{31} \cdot \mathbf{r}_{32} \left( \frac{1}{r_{31}^3} + \frac{1}{r_{32}^3} \right) \rangle + \frac{1}{2} \langle \frac{1}{r_{12}} \rangle = Q \langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{32}}{r_{31}^3} \rangle + \frac{1}{2} \langle \frac{1}{r_{12}} \rangle \quad (33)$$

The  $\langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{32}}{r_{31}^3} \rangle = \frac{1}{2} \left[ \langle \frac{1}{r_{31}} \rangle + \left( \langle \frac{r_{32}^2}{r_{31}} \rangle - \langle \frac{r_{32}^2}{r_{31}} \rangle \right) \right]$  expectation value can be computed either directly (see Table II), or with the use of the following relation

$$\langle \frac{\mathbf{r}_{32} \cdot \mathbf{r}_{31}}{r_{32}^3} \rangle = \frac{1}{Q} \langle p_1^2 \rangle - \frac{1}{2Q} \langle p_3^2 \rangle - \frac{1}{2Q} \langle \frac{1}{r_{12}} \rangle \quad (34)$$

since  $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle = \frac{1}{2} \langle p_1^2 \rangle + \frac{1}{2} \langle p_2^2 \rangle - \frac{1}{2} \langle p_3^2 \rangle$  and  $\langle p_1^2 \rangle = \langle p_2^2 \rangle$  in any two-electron system. All expectation values mentioned in the right-hand side of this equality can also be found in Table II. Analogous relations can be derived for the  $\langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{21}}{r_{31}^3} \rangle$  expectation value. Note that all expectation values in the right-hand side of Eq.(34) are regular, while the expectation value in the left-hand side of Eq.(34) contains the difference of the two singular expectation values  $\langle \frac{r_{31}^2}{r_{32}^3} \rangle$  and  $\langle \frac{r_{21}^2}{r_{32}^3} \rangle$ . As follows from Eq.(34) such a difference of these two singular expectation values is a regular value. This means that the two singular parts cancel each other completely. In general, an accurate numerical coincidence of the  $\langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{32}}{r_{31}^3} \rangle$  expectation values computed directly and with the use of Eq.(34) is another important test for our highly accurate wave functions. An analogous test can be used for the  $\langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{21}}{r_{31}^3} \rangle$  expectation value. It is also interesting to note that for the singlet states in two-electron ions the  $\langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{32}}{r_{31}^3} \rangle$  expectation values slowly vary with the nuclear charge  $Q$ . Moreover, these expectations values have a finite limit ( $\approx -0.1755$ ) when  $Q \rightarrow \infty$ .

## V. CONCLUSION

We have performed highly accurate computations of the excited  $2^1S(L=0)$ -states in the two-electron helium atoms:  ${}^\infty\text{He}$ ,  ${}^4\text{He}$  and  ${}^3\text{He}$ . The total energies and a large number of bound state properties have been determined for the  $2^1S$ -state in the  ${}^\infty\text{He}$ ,  ${}^4\text{He}$  and  ${}^3\text{He}$  atoms to very high numerical accuracy. By using our highly accurate variational wave functions we have also evaluated the expectation values of some singular operators. To the best of our knowledge this work is the first extensive study of the bound state properties

of the excited  $2^1S(L = 0)$ -states in two-electron helium atoms and most of the bound state properties computed in this work have never been evaluated in earlier studies. The knowledge of accurate expectation values given In Table II allows us to determine various lowest order relativistic, QED and mass corrections to the total energies of the  $2^1S$ -state(s) in the  ${}^\infty\text{He}$ ,  ${}^4\text{He}$  and  ${}^3\text{He}$  atoms.

In our extensive numerical calculations of the excited  $n^1S$ -states of the He atom(s) we have found no additional complications for our highly accurate procedure which is based on careful optimization of many non-linear parameters at small and intermediate dimensions. Briefly, this means that ‘instability problem’ mentioned in the Introduction is not critically important for our method. As follows from computational results obtained in this study our methods can also be used for highly accurate computations of the excited states in two-electron atoms and ions. In fact, we have performed some of such calculations. Table III contains our preliminary results for the total energies of the  $3^1S$ - and  $4^1S$ -states in the  ${}^\infty\text{He}$  atom. As follows from Table III the total energies of the  $3^1S$  and  $4^1S$  bound states converge very fast. Finally, our results from Table III for the the  $3^1S$ - and  $4^1S$ -states in the  ${}^\infty\text{He}$  atom are the most accurate total energies ever obtained for these states. It shows a great potential of our method for highly accurate computations of bound states in two-electron systems. In our test calculations of the bound  $5^1S$ -state in the  ${}^\infty\text{He}$  atom the short term booster function has not been constructed. Optimization of the three boxes for the non-linear parameters [8] allows us to produce a very compact (100-term) wave function which corresponds to the energy  $-2.0211768515145$  *a.u.* The difference with the ‘exact’ energy for this state is  $\approx 6.5 \cdot 10^{-11}$  *a.u.* Very likely, that further optimization of the non-linear parameters in the wave functions with 200 basis functions, Eq.(3), will produce the variational energy which is very close to the known energy for this state. Analogous situation can be found for other highly excited  $S$ -,  $P$ - and  $D$ -states in the  ${}^\infty\text{He}$  atom. In future studies we want to develop the new optimization strategy which can be used to chose the non-linear parameters in trial wave functions for highly excited  $S$ -,  $P$ - and  $D$ - states. This will allow us to produce very compact and highly accurate wave functions for these states. Computations with the use of very large wave functions ( $\geq 3000$  basis functions) can be avoided for highly excited bound states in two-electron atoms/ions. However, the current situation with highly accurate computations of highly excited singlet  $S$ -states (e.g., for the  $8^1S$ -,  $9^1S$ -,  $10^1S$ - and higher singlet  $S$ -states) in the helium atoms and helium-like ions

is far from satisfaction for our method, since the Hylleraas variational expansion (see, e.g., [4]) still provides better accuracy for such states (if comparable numbers of basis functions are used in both methods).

Note that our methods allow one to determine the total energies and many other bound state properties to very high numerical accuracy which is quite comparable and even better than analogous accuracy achieved for the ground states. The overall convergence rates observed in calculations of many bound state properties of the excited  $2^1S(L = 0)$ -states in two-electron helium atoms are relatively high. Briefly, this means that our optimization strategy used to optimize the non-linear parameters in highly accurate wave functions works very well for both ground and excited states in two-electron atoms/ions. This also contains the answer to the third problem mentioned in the Introduction that is the convergence rate for most of the bound state properties of the excited states is not substantially lower than for analogous properties of the ground state. Furthermore, the same optimization procedure has been applied to highly accurate computations of the  $2^1P(L = 1)$ - and  $2^3P(L = 1)$ -states in the He atom(s). The explicit form of the trial variational wave function for the states with  $L \geq 1$  is given in [8]. The best variational (total) energies obtained in our computations for these states in the  ${}^\infty\text{He}$  atom are: -2.1238430864981013590742 *a.u.* and -2.13316419077928320510251 *a.u.*, respectively [29]. Numerical uncertainties in these values can be evaluated as  $\approx 3.5 \cdot 10^{-20}$  *a.u.* In other words, these energies and corresponding wave functions are significantly more accurate than known from the modern literature (see, e.g., [2]).

Our highly accurate method can also be applied to highly accurate calculations of the weakly-bound singlet and triplet excited states in two-electron atoms and ions. These are the  $n^{1,3}S-$ ,  $n^{1,3}P-$ ,  $n^{1,3}D$ -states with  $n \geq 2$ . Results of these and other similar computations indicate clearly that clusterization of the wave functions plays a very important role for the excited states in two-electron atomic systems. The effect of clusterization for the exponential variational expansion was originally discovered in [30]. For our two-stage method [8] the clusterization of variational expansion, Eq.(3), means the presence of two following things. First, the short term (booster) wave function produces almost ‘exact’ energy already for  $N_0 = 200 - 300$ . For instance, for the  $3^1S(L = 0)$ -state the booster function with only  $N_0 = 200$  exponential basis functions allows one to obtain the total energy  $E = -2.061271989738157$  *a.u.* (current value), while the ‘exact’ energy of this state in the  ${}^\infty\text{He}$

atom is -2.061271989740911 *a.u.* Second, optimization performed at the second stage of our method produces a number (usually three) of ‘optimal’ parallelotops which are used later to chose parameters  $\alpha_i$ ,  $\beta_i$  and  $\gamma_i$  (where  $N_0 < i \leq N$ ) in Eq.(3). In actual calculations of the excited  $n^{1,3}S-$  and  $n^{1,3}P-$ states in the He atom(s) for  $n \geq 3$ , such an optimization of three parallelotops can be performed for  $N = 600$  in the total wave function. It produces almost the exact value of the bound state energy. Moreover, the optimal parallelotops for these bound states have almost degenerated structure. Briefly, this means that such parallelotops generate the wave function, Eq.(3), in which all parameters  $\gamma_i$  either equal zero exactly, or very close to zero. But this means that the role of electron-electron correlations (or  $r_{21}$  coordinate) rapidly decreases for highly excited bound states in two-electron ions [30]. In respect with this, the difference between the total energies of the triplet and singlet states with large angular moment  $L$  in He-like atoms and ions rapidly (almost exponentially) decreases, if the value of  $L$  increases. This remarkable property of the exponential variational expansion, Eq.(3), in applications to Rydberg states has been observed in all helium-like atoms and ions. It can be used to simplify future highly accurate computations of highly excited bound states in two-electron systems.

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### Appendix

The formula obtained by Racah, Rosenthal and Breit for the field shift is

$$E_M^{fs} = \frac{4\pi a_0^2}{Q} \cdot \delta(\mathbf{r}_{eN}) \cdot \frac{\gamma + 1}{\Gamma(2\gamma + 1)} \cdot B(\gamma) \cdot \left(\frac{2QR}{a_0}\right)^{2\gamma} \cdot \frac{\delta R}{R} \quad (35)$$

where  $Q$  is the nuclear charge,  $R$  is the nuclear radius and  $\gamma = \sqrt{1 - \alpha^2 Q^2}$ . For the helium atoms we have  $\gamma \approx 0.9998935$ . Therefore, to a very good accuracy one can assume that  $\gamma \approx 1$ . The factor  $B(\gamma)$  in Eq.(35) is

$$B(\gamma) = \frac{3}{(2\gamma + 1)(2\gamma + 3)} \approx \frac{1}{5} \quad (36)$$

It corresponds to the uniform distribution of the proton density over the volume of the nucleus. The ratio  $\frac{\delta R}{R}$  in the formula Eq.(35) equals unity, if the field shift is determined in

respect to the atom with a point nucleus. Now, in atomic units the formula Eq.(35) takes the form

$$E_M^{fs} = \frac{8\pi Q}{5} \cdot \delta(\mathbf{r}_{eN}) \cdot \left( \frac{R}{r_e} \frac{r_e}{a_0} \right)^2 \quad (37)$$

where  $r_e = \frac{e^2}{m_e c^2} = \alpha^2 a_0$  is the classical electron radius. Finally, we obtain the following formula for  $E_M^{fs}$

$$E_M^{fs} = \frac{8\pi Q}{5} \alpha^4 \cdot \delta(\mathbf{r}_{eN}) \cdot \left( \frac{R}{r_e} \right)^2 \quad (38)$$

This formula can slightly be modified to include other possible distributions of the proton density in the nuclei. The formula given in the main text contains an additional factor  $f(\lambda) = \frac{1+\frac{1}{3}\lambda}{1-\frac{1}{5}\lambda}$ . The formula Eq.(38) with such a factor (i.e. the formula Eq.(30) from the main text) also provides the correct answer in those cases when the uniform distribution of the proton density over the surface of the nucleus is assumed (in this case  $\lambda = 1$ ). Furthermore, variations of the parameter  $\lambda$  in Eq.(30) ( $0 \leq \lambda \leq 1$ ) allow one to describe other possible distributions of the proton density in light atomic nuclei with  $Q \leq 6$ .

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- [1] A.M. Frolov, J. Chem. Phys. **126**, 104302 (2007).
  - [2] A.M. Frolov, J. Phys. B **36**, 2911 (2003)
  - [3] Y. Accad, C.L. Pekeris and B. Schiff, Phys. Rev. A **4**, 1479 (1975).
  - [4] G.W.F. Drake, High Precision Calculations for Helium, in *Springer Handbook of Atomic, Molecular and Optical Physics* (2nd Ed., G.W.F. Drake Ed., Springer-Verlag, Berlin, 2006).
  - [5] H.A. Bethe and E.E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).
  - [6] S.T. Epstein, *The Variation Method in Quantum Chemistry*, (Academic Press, New York, 1974).
  - [7] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics. Non-relativistic Theory* (Butterworth-Heinemann, London, 1995), Chp. XVI.
  - [8] A.M. Frolov, Phys. Rev. E **64**, 036704 (2001).
  - [9] A.M. Frolov, J. Phys. A **40**, 6175 (2007).
  - [10] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
  - [11] R.T Pack and W. Byers Brown, J. Chem. Phys. **45**, 556 (1966).
  - [12] *The NIST Reference on Constants, Units and Uncertainty*, see:  
<http://physics.nist.gov/cuu/Constants/index.html>
  - [13] *CRC Handbook of Chemistry and Physics*, 85th Edition, Ed. D.R. Lide, (CRC Press, Inc., Boca Raton, Florida, 2004).
  - [14] V.A. Fock, Zs. Phys. **63**, 855 (1930).
  - [15] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I.A. Stegun, (Dover, New York, 1972).
  - [16] I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products*, 5th Ed. edited by A. Jeffrey, (Academic Press, New York, 1994).
  - [17] A.M. Frolov, J. Phys. B **38**, 2723 (2005).
  - [18] F.A. Harris, A.M. Frolov and V.H. Smith, Jr., J. Chem. Phys. **121**, 5323 (2004).
  - [19] I.I. Sobel'man, *Atomic Spectra and Radiative Transitions* (Springer-Verlag, Berlin, 1979), Ch. 6.
  - [20] C. Froese Fisher, T. Brage and P. Jönsson, *Computational Atomic Structure* (IOP Publishing

Ltd., London, 1997), Ch. 8.

- [21] W.H. King, *Isotope Shifts in Atomic Spectra*, (Plenum Press, New York, 1984).
- [22] A.M. Frolov, J. Chem. Phys. **124**, 224323 (2006).
- [23] J.S. McCarthy, I. Sick and R.R. Whitney, Phys. Rev. C **15**, 1396 (1977).
- [24] G. Carboni, G. Gorini, G. Torelli, L. Palffy, F. Palmonari and E. Zavattini, Nucl. Phys. A **278**, 381 (1977).
- [25] L.R.B. Elton, *Nuclear Sizes* (Oxford Library of the Physical Sciences, Oxford-Clarendon, Oxford, 1968).
- [26] R.G. Barret and D.F. Jackson, *Nuclear Sizes and Structures*, (Clarendon Press, Oxford, 1977).
- [27] K. Pachuki and J. Sapirstein, J. Phys. B **33**, 455 (2000).
- [28] J.P. Vinti, Phys. Rev. **58**, 882 (1948).
- [29] A.M. Frolov and D.M. Wardlaw, Phys. Rev. A **81**, 062504 (2010).
- [30] A.M. Frolov, Opt. Specrtrosk. **61**, 732 (1986) [Opt. Spectr. (USSR) **61**, 1171 (1986)].

TABLE I: The total non-relativistic energies  $E$  and  $\langle r_{21} \rangle$ ,  $\langle \delta_{31} \rangle$ ,  $\nu_{31}$  expectation values computed for the excited  $2^1S(L=0)$ -states of the  ${}^\infty\text{He}$  atom (in atomic units).

$N$	$E({}^\infty\text{He})$	$\langle r_{21} \rangle$	$\langle \delta_{31} \rangle$	$\nu_{31}$
1500	-2.145 974 046 054 416 890 40	5.26969620234182140	1.3094607823	-2.0000000848
2000	-2.145 974 046 054 417 174 01	5.26969620234181075	1.3094607799	-1.9999999787
2500	-2.145 974 046 054 417 298 64	5.26969620234180607	1.3094607811	-2.0000000487
3000	-2.145 974 046 054 417 342 16	5.26969620234180443	1.3094607802	-1.9999999798
3500	-2.145 974 046 054 417 372 44	5.26969620234180331	1.3094607801	-1.9999999784
4000	-2.145 974 046 054 417 385 25	5.26969620234180281	1.3094607802	-1.9999999977
4200	-2.145 974 046 054 417 391 41	5.26969620234180258	1.3094607804	-2.0000000089
$\infty^{(a)}$	-2.145 974 046 054 417 415(10)			-2.0
	-2.145 974 046 054 419(6) <sup>(b)</sup> [4]			
	-2.145 974 04(1) <sup>(b)</sup> [3]			

<sup>(a)</sup>The asymptotic value of the total energy (in *a.u.*)

<sup>(b)</sup>The best variational results known from earlier calculations [4] and [3] in atomic units.

TABLE II: The bound state properties  $X$  computed for the excited  $2^1S(L=0)$ –state in the  ${}^\infty\text{He}$ ,  ${}^4\text{He}$  and  ${}^3\text{He}$  atoms (in atomic units).

$X$	${}^\infty\text{He}$	${}^4\text{He}$	${}^3\text{He}$
$E$	-2.14597404605441739141	-2.14567858758314906950	-2.14558192369821233185
$\langle T \rangle$	2.14597404605441739081	2.14567858758314906890	2.14558192369821233125
$\langle V \rangle$	-4.29194809320883477957	-4.29135717516629813451	-4.29116384739642465859
$\eta$	$4.571 \cdot 10^{-19}$	$7.8674 \cdot 10^{-19}$	$9.1373 \cdot 10^{-19}$
$\langle r_{31}^{-2} \rangle$	0.1437248133044633	0.1436882345740985	0.1436762703243981
$\langle r_{21}^{-2} \rangle$	4.1469390197898792	4.1458017822058179	4.1454297481103379
$\langle r_{31}^{-1} \rangle$	1.13540768612560041	1.13525123516046493	1.13520005025470815
$\langle r_{21}^{-1} \rangle$	0.24968265239356710	0.24964776547556185	0.24963635362241032
$\langle \frac{1}{r_{21}r_{31}r_{32}} \rangle$	0.39836585186133074	0.39819906128376390	0.39814450960354474
$\langle \frac{1}{r_{21}r_{31}} \rangle$	0.34063384586003005	0.34053958784463326	0.34050875587573647
$\langle \frac{1}{r_{31}r_{32}} \rangle$	0.56186146745960207	0.5617029565988612	0.56165110690333470
$\frac{1}{2} [\langle \frac{r_{32}}{r_{31}} \rangle - \langle \frac{r_{21}}{r_{31}} \rangle]$	-0.625372574195182710	-0.625157759769931583	-0.625087487579971712
$\langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{32}}{r_{31}} \rangle$	-0.0576687311323827964	-0.0575321421896994047	-0.0574874624526176361
$\langle \frac{\mathbf{r}_{31} \cdot \mathbf{r}_{21}}{r_{31}} \rangle$	1.19307641725798262375	1.19278337735016376067	1.19268751270732578757
$\langle r_{31} \rangle$	2.973061134389489243	2.973491187710339638	2.973631893971735653
$\langle r_{21} \rangle$	5.269696202341802818	5.270450917235814928	5.270697843066571909
$\langle r_{31}^2 \rangle$	16.08923324404050295	16.09391391074115758	16.09544547281748570
$\langle r_{21}^2 \rangle$	32.30238037187441050	32.31159744722066081	32.31461335707651003
$\langle r_{31}^3 \rangle$	108.06042106146845	108.10756711191265	108.12299522961221
$\langle r_{21}^3 \rangle$	224.03043954850232	224.12604278314834	224.15732795934735
$\langle r_{31}^4 \rangle$	825.75317813369571	826.23293858862828	826.38995080810075
$\langle r_{21}^4 \rangle$	1737.415292784614	1738.402036368951	1738.724968194081
$\tau_{31}$	0.557144578327034669	0.557137512037319818	0.557135200602530583
$\tau_{21}$	-0.014657043357177236	-0.014643315290865667	-0.014638824110935725
$\langle f \rangle$	$2.49080283242230255 \cdot 10^{-2}$	$2.49079271959434924 \cdot 10^{-2}$	$2.49078942735313599 \cdot 10^{-2}$
$\langle -\frac{1}{2} \nabla_1^2 \rangle$	1.0729870230272085694	1.0726915861654766111	1.0725949387331539546
$\langle -\frac{1}{2} \nabla_3^2 \rangle$	2.1554779104737081945	2.1548473559242290248	2.1546410836274219596
$\langle \mathbf{p}_1 \cdot \mathbf{p}_3 \rangle$	-2.1554779104737081945	-2.1548473559242290248	-2.1546410836274219596
$\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$	$9.5038644192910556894 \cdot 10^{-3}$	$9.4641835932758026973 \cdot 10^{-3}$	$9.4512061611140503550 \cdot 10^{-3}$
$\langle \mathbf{r}_{21} \cdot \mathbf{r}_{31} \rangle$	16.1511901859372052475	16.1557987236103304049	16.1573066785382550123
$\langle \mathbf{r}_{31} \cdot \mathbf{r}_{32} \rangle$	$-6.195694189670229434 \cdot 10^{-2}$	$-6.188481286917282672 \cdot 10^{-2}$	$-6.186120572076931285 \cdot 10^{-2}$
$\langle \delta(\mathbf{r}_{31}) \rangle$	1.3094607802	1.3089223177	1.3087461812
$\nu_{31}$	-1.99999997659	-1.999725848502	-1.999636146310
$\nu_{31}^a$	-2.0	-1.999725850875267686059	-1.999636157582479619549
$\langle \delta(\mathbf{r}_{21}) \rangle$	$8.648433654 \cdot 10^{-3}$	$8.645119901 \cdot 10^{-3}$	$8.644035949 \cdot 10^{-3}$
$\nu_{21}$	0.4999998171	0.4999994703	5.0000004784
$\nu_{21}^a$	0.5	0.5	0.5
$\langle \delta_{321} \rangle$	0.1755555002	0.1753991714	0.1753446276
$\langle r_{21}^{-3} \rangle_R$	-0.04073283492915455	-0.04069706227378580	-0.04068536285394055
$\langle r_{31}^{-3} \rangle_R$	-39.23799206891561	-39.21960245645624	-39.21358724048685
$\langle r_{21}^{-3} \rangle$	0.06794658607018129	0.06794071686462781	0.06793879648060461
$\langle r_{31}^{-3} \rangle$	-22.78226037360592	-22.7711995110946440	-22.6896828517925066

(a) The exact value.

TABLE III: The total non-relativistic energies  $E$  (preliminary results) of some excited  $n^1S(L = 0)$ -states ( $n = 3, 4$ ) of the  ${}^\infty\text{He}$  atom (in atomic units).

$N$	$E(3^1S\text{-state})$	$E(4^1S\text{-state})$
1500	-2.061 271 989 740 906 234	-2.033 586 717 030 718 055
2000	-2.061 271 989 740 907 482	-2.033 586 717 030 722 441
2500	-2.061 271 989 740 907 999	-2.033 586 717 030 723 921
3000	-2.061 271 989 740 908 266	-2.033 586 717 030 724 515
3500	-2.061 271 989 740 908 387	-2.033 586 717 030 724 857
3800	-2.061 271 989 740 908 430	-2.033 586 717 030 725 074
$\infty^{(a)}$	-2.061 271 989 740 908 48(5)	-2.033 586 717 030 725 20(7)
[4] <sup>(b)</sup>	-2.061 271 989 740 911(5)	-2.033 586 717 030 72(1)

<sup>(a)</sup>The asymptotic value of the total energy (in *a.u.*)

<sup>(b)</sup>The best variational results known from earlier calculations [4] in atomic units.